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(54) Title: PACKAGING LAMINATE WITH GAS AND AROMA BARRIER PROPERTIES

(57) Abstract

A packaging laminate having at least one layer of a substrate coated with a carbon containing silicon oxide is disclosed herein. A method for producing the laminate, and blanks and packages fabricated from the laminate are also disclosed herein. The PECVD process of the present invention strains the substrate film during deposition thereby creating a very thin oxide layer with superior oxygen and aroma barrier properties. The carbon–containing silicon oxide coating has a stoichiometery of SiOxCy in which x is within the range of 1.5–2.2 and y is within the range of 0.15–0.80. The substrate film may be composed of a material selected from the group consisting of paper, paperboard, a foamed core, polyethylene terephthlate, polyamide, polyethylene and polypropylene.

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TITLE

PACKAGING LAMINATE WITH GAS AND AROMA BARRIER PROPERTIES

Technical Field

The present invention relates to a packaging laminate for the packaging of liquid food products. Specifically, the present invention relates to a barrier packaging laminate having increased ductility, a process for manufacturing the laminate, and a packaging container and blank fabricated from the packaging laminate.

Background Art

Packaging laminate materials having flexibility have been used for packaging liquid food products for many years. For example, milk has been packaged in cartons made from a laminate composed of a paperboard substrate with thermoplastic coatings on both surfaces. The surfaces of the carton are heat-sealed together to form a desired shape such as a gable top carton.

Some food products, such as orange juice, packaged in such cartons lose their nutritional values due to the permeation of oxygen through the carton walls. One solution has been to include an aluminum foil layer with the laminate material to reduce the permeation of oxygen through the walls, and to minimize the degradation of the nutrients such as vitamin C (ascorbic acid). Although aluminum foil is effective as a barrier material, its use in cartons raises environmental concerns. Various attempts have been made to develop practical alternatives to aluminum foil that possess excellent oxygen and aroma barrier properties, and are easily disposable after consumption of the product contained therein.

Another problem in the packaging of liquid food products in cartons arises from the structure of the carton. The carton is fabricated from a carton blank (composed of a laminate such as the ones discussed above) that is folded along one or more crease lines for formation into the desired carton shape. In general, portions of the blank are overlapped for sealing which may be accomplished by the application of suitable adhesive or by heat-sealing the thermoplastic layers together. The creasing of the laminate material, as above mentioned, to create the blank imposes stresses on the laminate material. These stresses have the possibility of causing leakage or at least weakening of the laminate material so that subsequent handling of the carton may lead to leakage.

New oxygen barrier materials have emerged from recent developments in plasma enhanced deposition technology for plastic films. The food and pharmaceutical packaging industries have shown tremendous interests in substrate (usually polyester) films coated with a thin silicon oxide layer. These materials show excellent tolerance to the thermo-mechanical stresses encountered during the various conversion processes of the raw materials to the final carton. US patent No. 4,888,199 describes a process of depositing a thin film on a surface with the use of plasma under controlled conditions.

During these processes, a major concern is the durability of the barrier layer in that it must not crack or delaminate (detach) from the substrate film. Crack is controlled by the cohesion of the oxide material to itself, whereas delamination is controlled by the interfacial adhesion between the oxide material and the substrate film. Thus, there remains a need for a silicon oxide coated substrate that is resistant to cracking and delamination.

Disclosure of the Invention

In view of the deficiencies of conventional barrier laminate materials, it is a primary object of the present invention to provide a packaging laminate material having greater barrier and durability properties than conventional barrier laminate materials.

It is an additional object of the present invention to provide a flexible package composed of the laminate material that is readily capable of being formed, filled and sealed on conventional packaging machines.

It is yet an additional object to provide a packaging laminate material that may be readily disposed without detriment to the environment.

It is yet an additional object to improve the durability to thermo-mechanical stresses encountered during various conversion processes of the raw materials to the final carton.

These objects are accomplished by a laminate material composed of substrate material with a plasma-enhanced vapor deposition of silicon oxide thereon. The deposited silicon oxide is a carbon-containing silicon oxide coating with the following formula SiOxCy wherein x is within the range of 1.5-2.2 and y is within the range of 0.15-0.80, and more preferably x is within the range of 1.7-2.1 and y is within the range of 0.39-0.47. However, the oxide coating may not be limited to these three elements due to impurities occurring throughout the manufacturing process of the laminate. The silicon oxide is formed in a plasma discharge that contains a gas mixture of oxygen, helium and organic silicon compounds (precursor compounds that contain carbon). During the plasma discharge reaction, some of the carbon atoms from the organic silicon compounds are incorporated into the deposited layer while other carbon atoms are exhausted from the system as various gaseous hydrocarbons.

Plasma-enhanced chemical vapor deposition is a known technique for fabricating silicon oxide coated substrate films. The present invention improves upon that technique by straining the substrate film during deposition and controlling the quantity of oxygen in the gas mixture to create an oxide with the proper stoichiometry.

Brief Description of the Drawings

Fig. 1 schematically illustrates an example of the device for plasma CVD of according to this invention.

Fig. 2 schematically illustrates an example of the device for plasma CVD of according to this invention.

Fig. 3 schematically illustrates an example of the packaging blank having the laminate according to this invention.

Fig. 4 schematically illustrates the packaging laminate according to the first embodiment of the invention .

Fig. 5 schematically illustrates the packaging laminate according to the second embodiment of the invention .

Fig. 6 schematically illustrates the packaging laminate according to the third embodiment of the invention .

Fig. 7 schematically illustrates the packaging laminate according to the fourth embodiment of the invention .

Fig. 8 schematically illustrates the packaging laminate according to the fifth embodiment of the invention.

Fig. 9 schematically illustrates the packaging laminate according to the sixth embodiment of the invention.

Fig. 10 schematically illustrates the packaging laminate according to the seventh embodiment of the invention.

Fig. 11 schematically illustrates an embodiment in which the silicon oxide layer is in direct contact with the products in the interior of the package.

Fig. 12 is a graph showing fragmentation process of the oxide coating by the plasma CVD in the Evaluation Example according to this invention and the Prior Arts Example.

Best Mode(s) of Carrying Out The Invention

Figs. 1 and 2 illustrate devices capable of manufacturing the packaging laminate of the present invention. These devices 200 and 200a each consists of a vacuum chamber 202 forming the process zone, a pump 204 connected to the chamber 202, means for introducing the precursor gas mixture, a dram, an unwinding roll 206 for feeding the substrate film to the vacuum chamber 202 and a rewinding roll 208 for pulling film from the chamber 202. A PECVD method is more thoroughly described in US patent No. 5,224,441, which is hereby incorporated into this specification by reference.

Electric motors may be used for the unwinding roll 206 and the rewinding roll 208. The motors allow for control of the strain (tensioning force) on the substrate film. In practicing the present invention, the substrate film is strained in a range having an upper limit prior to the plastic deformation of the substrate film as determined by the Young modulus of the substrate, and a lower limit of an improvement in the cohesion force of the oxide coating, and an adhesion force between the oxide coating and the

substrate film. If the dram is absent, the straining of the substrate during vapor-deposition is still applied in a similar manner.

For example, a gas mixture of oxygen, an inert carrier gas (such as helium) and a vaporized organic silicon compound such as tetra-methyl disiloxane (TMDSO) or hexamethyl disiloxane (HMDSO) is fed into the vacuum chamber. When the plasma is ignited, the vaporized silicon compound reacts with the oxygen to form a silicon oxide compound. The compound is deposited on and chemically bonded to the cool substrate film in the vacuum chamber 202.

By regulating the quantity of oxygen in the gas mixture that is fed into the vacuum chamber 202, it is possible to control the chemical reaction within the vacuum chamber so that the thus-formed silicon oxide can have a formula SiOxCy, in which x is within the range of 1.5-2.2 and y is within the range of 0.15-0.80, and more preferably x is 1.7-2.1 and y is within the range of 0.39-0.47. The carbon-containing silicon oxide coating of the present invention has superior oxygen and aroma barrier properties.

Using an ESCA method, the carbon-containing silicon oxide coating of the present invention has an average atom concentration 30.1 ± 5.0% of silicon, 57.3 ± 5.0% of oxygen, 12.6±5.0% of carbon. From a stoichiometric perspective, the carbon containing silicon oxide has a average stoichiometry of $SiOx_{1.90}C_{0.419}$.

The carbon-containing silicon oxide coating is obtained by vapor-depositing onto the substrate film via PECVD method while straining the substrate film within range set forth above. The silicon oxide compound is directly formed on the surface of the substrate. The compactness of the thus-formed silicon oxide layer on the substrate or the core layer becomes sufficiently high from a barrier perspective once the strained substrate film is released or no longer under the tensioning force. As a result of this

process, the silicon oxide layer can be made very thin without any loss of the desired barrier properties.

The preferred substrate is a flexible thermoplastic material, such as polyethylene, polypropylene or polyethylene terephthalate (PET).

The silicon oxide layer formed by the PECVD method according to this invention is able to withstand substantial elongation without rupture. This characteristic is important for use of the laminate material in the packaging of liquid food products since the typical packaging laminate material has crease lines formed in the surface of the laminate to facilitate the folding of the material into a package.

The ability of the silicon oxide layer to be deformed without rupture substantially decreases the possibility of leakage along the crease lines.

A packaging blank 2 formed from the continuous web of the laminate material is shown in Fig. 4. As shown in Fig. 4, crease lines 3 are stamped, or otherwise impressed into the surface that is to become the inner surface of the carton. The laminated blanks 2 have a core layer of paper or paperboard, a barrier layer, an inner products contact layer of low-density polyethylene (LDPE) and an outer thermoplastic material layer of LDPE.

Crease lines cause indentations generally in the inner LDPE layers, in the barrier layers and in the core layer. After the blanks are folded into the cartons and closed, the seal portion 8, as shown in Fig. 4, is sealed by heat at temperatures ranging from 121°C to 260° in order to bond the inner and outer LDPE layer portions 8 together. The blanks 2 are cut from each other at the cutting portion 9 and separated into individual packaging blanks 2.

The silicon oxide coatings obtained from the plasma CVD method according to this invention have a higher ductility than silicon oxide coatings formed by the concentional plasma CVD method. The packaging laminate materials of the present

invention may be folded and heat-sealed on a conventional packaging machine without cracks and/or holes appearing in the barrier layer.

It is desirable to make the silicon oxide coating thin since it allows the coating process to proceed faster. Also, a thick coating on the substrate tends to cause curling of the laminate that makes later fabrication more difficult than with a thin coating. Specific additional layers should be included in order to utilize the barrier layer produced in the plasma enhanced chemical vapor deposition process as a packaging laminate for food products.

A preferred embodiment of the packaging laminate material according to this invention is shown in Fig. 4. Laminate 10 comprises two prefabricated laminates 10a and 10b that are bonded to one another by an intermediate layer 11 of adhesive. The 1st laminate material 10 has a rigid but foldable core layer of paper or paperboard 12, and two outer layers 13 and 14 of LDPE which are heat-sealable.

The 2nd laminate material 10b has a substrate or carrier layer 15 on which a thin carbon-containing silicon oxide layer 16 has been deposited by the PECVD method. The layer 16 acts as oxygen and aroma barrier. The carbon-containing silicon oxide layer 16 deposited on the substrate or the carrier layer 15 by the PECVD method has the thickness of between 50-500Å, with a preferred thickness of about 200 Å or 193 Å. The thickness imparts oxygen and other desired barrier properties to the packaging laminate material 10.

The substrate or carrier layer 15 is a flexible thermoplastic material, which is heat-sealable, at temperatures between 121°C - 260°C, to the LDPE layer 13 to produce packaging for liquid food products. For example, the carrier layer 15 may be formed from LDPE. The packaging laminate 10 is produced by bonding together the first laminate 10a and the second laminate 10b with the adhesive 11 which is applied

between the webs for permanent bonding of the webs for the formation of the finished packaging laminate 10.

Fig. 5 shows another embodiment of the packaging laminate according to the invention for producing a package possessing superior oxygen and aroma barrier properties. The packaging laminate 20 comprises a 1st laminate unit 20a and a 2nd laminate unit 20b which are bonded to one another by an intermediate adhesive layer 21. The 1st laminate unit 20a comprises a rigid but foldable layer 22 of paper or paperboard and outer LDPE layers 23 and 24.

The 2nd laminate material unit 20b has a substrate or carrier layer 25. For example, the layer may consists of a flexible plastic such as polyethylene terephthalate (PET), amorphous polyester, biaxially oriented polyester or polypropylene. On its side facing the laminate units 20a, the substrate or the carrier layer is coated with the oxygen and aroma barrier layer 26 which comprises a carbon containing silicon oxide. The carbon-containing silicon oxide has a formula SiO_xC_y in which x is within the range of 1.7-2.1 and y is within the range of 0.39-0.47.

The other side of the substrate or carrier layer 25 has an outer layer 27 of thermoplastics. The layer 27 is heat-sealable, at a temperature between 121°C-260°C, with the thermoplastic outer layer 23 of the laminate 20a, and is bonded to the substrate or carrier layer 25 with the aid of an intermediate adhesive 28.

In the laminate material 20 of the embodiment, the carbon-containing silicon oxide layer acting as an oxygen and aroma barrier is produced by the PECVD method of the present invention and has a thickness of 50-500Å, preferably 100-200Å, more preferably 200Å, and even more preferably a thickness of 193Å. This thickness is enough to impart the desired oxygen and aroma barrier properties to the packaging container produced from packaging laminate material.

The packaging laminate 20 may be produced by bonding together the prefabricated web of the laminate unit 20a and the prefabricated web of the laminate unit 20b by means of an adhesive layer which is applied between the two webs for the formation of the finished packaging laminate 20.

Fig. 6 shows a further embodiment of a packaging laminate of the present invention for producing a folded and sealed package possessing superior oxygen and aroma barrier properties. The packaging laminate material 30 comprises a first laminate unit 30a and a second laminate unit 30b which are permanently bonded to one another by an intermediate adhesive layer 31. The 1st laminate unit 30a comprises a rigid but foldable layer 32 of paper or paperboard and outer thermoplastic surrounding layers 33 and 34.

The second laminate unit 30b comprises a substrate or carrier layer 35 of plastic which, on its side facing away from the laminate unit 30a, is coated with a layer 36 acting as oxygen and aroma barrier and consisting of a silicon oxide of the general chemical formula SiOx in which x may vary within 1.7-2.1 and y may vary within 0.39-0.47. The silicon oxide layer 36 is covered by an outer layer of thermoplastic 38 which is heat-sealable with the thermoplastic in the outer thermoplastic layer 33 of the laminate unit 30a and which is bonded to the silicon oxide layer 36 by the intermediary of the intermediate adhesive layer 38. Alternatively, another method of forming the laminate 30 is by coextruding the layers 31 and 34 to layers 35 and 36, and then coextruding layers 37 and 38 against this laminate.

In the laminate of this embodiment, the carbon-containing silicon oxide layer 36 is produced according to the present invention and which has shown superior oxygen and aroma barrier properties for packaging containers produced from the packaging laminate 30.

Fig. 7 shows a further embodiment of a packaging laminate according to the present invention for producing a folded and sealed package possessing superior oxygen and aroma barrier properties.

The packaging laminate 40 comprises a first laminate unit 40a and a second laminate unit 40b which are permanently bonded to one another by an intermediate adhesive layer 41.

The first laminate unit 40a includes a rigid but foldable core layer 42 of a heat-sealable plastic material, e.g., foamed or expanded polyethylene, foamed or expanded polypropylene, formed or expanded polyester, or mineral-filled polypropylene, and an outer surrounding layer 43 of heat-sealable thermoplastic that is capable of being bonded to the core layer 42 by heat sealing.

The second laminate unit 40b comprises a substrate or carrier layer 44 of a thermoplastic which is heat-sealable to the outer thermoplastic layer 43 or the core layer 42 of the first laminate unit 40a, e.g., polyester or polypropylene, and which, on its side facing the first laminate unit 40a, carries a layer 45 acting as an oxygen and aroma barrier, and consisting of a silicon oxide of the formula SiOxCy in which x may vary within 1.7-2.1 and y may vary within 0.39-0.47.

In the laminate 40 of the embodiment, the carbon-containing silicon oxide layer 45 acting as an oxygen and aroma barrier is produced by the PECVD method of the present invention and has a thickness of 50-500Å, preferably 100-200Å, more preferably 200Å, and even more preferably a thickness of 193Å. This thickness is sufficient to impart the desired oxygen and aroma barrier properties to a packaging container produced from packaging laminate 40.

Fig. 8 schematically illustrates a packaging laminate 50 according to the present invention for producing a package of the bag type, without a paper or paperboard core layer. The packaging laminate 50, comprises a first prefabricated laminate unit or

flexible plastic film 50a and a second prefabricated laminate unit 50b which are permanently bonded to one another by an intermediate adhesive layer 51.

The first laminate unit or plastic film 50b consists of a single layer of a flexible heat-sealable thermoplastic, e.g., polyester, polyethylene or polypropylene, that is capable of being heat-sealed at a temperature of 121°C-260°C in a conventional heat-sealing machine.

The second laminate unit 50b comprises a substrate or carrier layer 52 which, on its side facing the laminate unit 50a, is coated with a layer 53 acting as an oxygen and aroma barrier and consisting of a silicon oxide of the general chemical formula SiOxCy in which x may vary within 1.7-2.1 and y may vary within 0.39-0.47.

The substrate or carrier layer 52 consists of a thermoplastic, which is flexible and heat-sealable at a temperature between 121-260°C to the thermoplastic layer in the first laminate unit. For example, the carrier layer 52 may be formed of polyester, polyethylene or polypropylene. In the laminate 50 of the embodiment, the carbon-containing silicon oxide layer 53 acting as an oxygen and aroma barrier is produced by the PECVD method of the present invention, and has a thickness of 50-500Å, preferably 100-200Å, more preferably 200Å, and even more preferably a thickness of 193Å. This thickness is enough to impart the desired oxygen and aroma barrier properties to the packaging container produced from packaging laminate 50.

The packaging laminate 50 is produced by bonding the thermoplastic layer of the first laminate unit 50a to the second laminate layer 50b by means of an adhesive layer 51 which is applied between the two units. The laminate 50 may be formed into packages as described above, including forming crease lines in the inner layer 50a and practically into the barrier layer 53. These crease lines facilitate folding of the laminate along predetermined lines. Since all of the layers of the laminate 50 are flexible, this laminate can be used to produce a flexible wall package.

Fig. 9 schematically illustrates a packaging laminate according to the present invention for producing a sealing strip for use in a packaging container. The packaging laminate 60 compresses a first laminate unit 60a and a second laminate unit 60b which have been permanently bonded to one another by an intermediate adhesive layer 61. The first laminate unit 60a is formed of polyethylene . The second laminate unit 60b comprises a substrate or carrier layer 62 of plastic, e.g., polyester , biaxially oriented polyester or polypropylene .

The layer 62, on its side facing away from the first laminate unit 60a, is coated with a layer 63 acting as an oxygen and aroma barrier and consisting of a silicon oxide of the general chemical formula SiO_xC_y in which x may vary within 1.7-2.1 and y may vary within 0.39-0.47.

The carbon-containing silicon oxide layer 63 is covered by an outer layer of thermoplastic 64, e.g., polyethylene, which is bonded to the silicon oxide 63 by an intermediate adhesive layer 65. The carbon containing silicon oxide layer 63 is produced by the PECVD method of the present invention, and has a thickness of about 200Å, and more preferably a thickness of 193Å which is enough to impart the desired oxygen and aroma barrier properties to the packaging container produced from packaging laminate 60. The packaging laminate 60 is produced by bonding the thermoplastic layer of the first laminate unit 60a to the second laminate layer 60b by means of an adhesive layer 61 which is applied between the two units.

Fig. 10 shows a packaging laminate according to the invention for producing a package laminate that possesses superior oxygen gas and aroma barrier properties. The packaging laminate 70 comprises a first laminate unit or plastic film 70a and a second laminate unit 70b which are permanently bonded to one another by an intermediate adhesive layer 71. The first laminate unit 70a comprises a flexible or foldable

thermoplastic material, foamed or expanded polypropylene , foamed or expanded polyester or mineral-filled polypropylene .

The second laminate unit 70b comprises a substrate or carrier layer 72 of thermoplastic that is heat-sealable with the thermoplastic in the first laminate unit 70a. The side of the second laminate unit 70b that faces the first laminate unit 70a, is coated with a layer 73 acting as an oxygen and aroma barrier, and consisting of a silicon oxide of the general chemical formula SiO_xC_y in which x may vary within 1.7-2.1 and y may vary within 0.39-0.47.

The silicon oxide layer 73 is produced by plasma enhanced chemical vapor deposition and has a thickness of about 200Å, more preferably 193Å, which imparts to the packaging laminate 70 the desired oxygen and aroma barrier properties. The packaging laminate 70 may be produced by bonding together the first laminate unit 70a and the second laminate unit 70b by means of an intermediate adhesive layer 71 which is applied between the units.

Fig. 11 shows an embodiment in which the carbon containing silicon oxide layer is in direct contact with the products in the interior of the package. In this embodiment, the packaging laminate 80 includes a base layer 81, which may be any suitable material that is flexible, such as paper, foam core, PET, polyamide, polyethylene, or polypropylene .

The exterior side of the base layer 81 is coated with an LDPE layer 82. On the interior side of the base layer, a layer of LDPE 83 has a thin coating 84 of the carbon-coating silicon oxide, as described above with respect to the layers 15 and 16 of Fig. 4. The LDPE 83 may be bonded to the base layer by a suitable adhesive. Since the carbon-containing silicon oxide layer 84 is exposed on the interior side of the laminate when the laminate is folded and heat-sealed to form a container, the carbon-containing silicon oxide layer 84 will be in direct contact with the contents of the container.

When the laminate is used for a food product container, the carbon-containing silicon oxide layer 84 is an acceptable material for this purpose, since it would have no deleterious effect on the food contents. Due to the thickness of the carbon-containing silicon oxide 84, a strong heat seal bond can be formed between the exterior layer 82 and the interior layer 83 when the laminate is folded and formed in conventional packaging materials at a heat sealing temperature of between 121-260°C. Another way to form a bond using the packaging laminate 80 is to employ ultrasonic heating which cause softening of the LDPE layer 83 without requesting the transmission of heat through the carbon-containing silicon oxide layer 84.

As an example of a preferred packaging laminate in accordance with the embodiment to Fig. 11, the exterior LDPE layer should have a thickness of about 15 microns and the interior LDPE layer should have a thickness of about 15 microns. The base layer 81, if present, should have a thickness of between 15 microns and 200 microns. The carbon-containing silicon oxide layer 84 should have a thickness of between 50 and 500Å.

A laminate having layers of these thicknesses will have good barrier properties and will be capable of being formed into packages by heat-sealing without causing holes or tears that might cause the packages to leak. Thus, in practicing the present invention, a packaging laminate may be produced possessing excellent oxygen and aroma barrier properties without attendant problems and drawbacks of the type inherent in the prior art technology, for example the laminate disclosed in European Patent Application number 0 378 990.

In particular, there will be realized a packaging laminate including a carbon-containing silicon oxide produced by chemical plasma vapor deposition and, even at such slight thickness as 193Å, making possible the production, by fold formation, of a packaging container possessing superior oxygen gas and aroma barrier properties.

While the invention has been described above with reference to specific laminate structures, it is, naturally, not restricted exclusively to such structures. Without departing from the spirit and scope of the inventive concept as defined in the appended claims, it is possible, and obvious to a person skilled in the art, to select other materials in respect of both the substrate or the carrier layer and the core layer than those specifically disclosed herein. For example, it is possible, within the purview of the inventive concept as herein disclosed, to employ as a material for the substrate or carrier layer, a layer of greaseproof paper, where desired.

The laminate material of this invention has a gas-barrier layer that is effective in thickness as low as 50Å, and in a preferred thickness of 200Å. The advantage of the thin coating resides principally in the excellent mechanical properties that are related to their lower internal stresses. Such thin coatings provide better resistance to cracking which is particularly important for containers formed by creasing and folding, as described in this specification.

The corners and folded edges of such containers are particularly sensitive areas and the use of materials with thicker coatings will result in cracks in these parts of the package and consequent loss of barrier properties. In contrast, the thin coatings as disclosed in this application are sufficiently flexible and extensible to make possible a conversion of the material to packing containers without any danger of cracking or breaking even in the most exposed areas. The lower internal stress of the thin coatings are also reflected in the property that these materials do not curl. Thick coatings on plastic films may cause additional problems during subsequent processing to produce laminates.

It should finally be observed that a packaging laminate according to the invention, in addition to superior oxygen and aroma barrier properties, also possesses the advantage that it is of the non-scalping type. As a result, the silicon oxide layer of

the packaging laminate can be employed in direct contact with package contents which-are particularly storage-sensitive, such as fruit juice, without "scalping" or impoverishing the contents of its aromatic flavorings, essential oils, which occur in generous quantities in this type of contents.

Examples

Various processes for utilizing the PECVD method to form thin films on the substrate are known. The plasma is formed in the enclosed reaction chamber, in which the substrate is positioned to deposit thin film on the surface. The above-mentioned substrate can be formed from metal, glass or certain plastics. The air is pumped out of the chamber until a high degree of vacuum is achieved in the chamber.

For example, an organic silicon compound, such as hexamethyl disiloxane, is introduced into the chamber with the oxygen and the helium, so that those silicon molecule and oxygen molecules are deposited on the surface of the substrate. The resulting film is described in US patent No. 4,888,199 as being a thin film that is very hard, scratch-resistant, optically clear, adheres well to a flexible substrate. The disclosure of the patent is hereby incorporated into this specification by reference. In the process mentioned in the '199 patent, the substrate deposited with the silicon oxide is maintained at a temperature of about 10-35°C, preferably 15-25°C and the substrate may be formed from polyethylene terephthalate (PET) or polycarbonate resin. In the '199 patent, the thickness of the silicon oxide film is 100 Å (Angstrom) – about 400 Å and the thickness of the substrate is 1.5 microns – 250 microns.

While pre-straining a substrate film according to this invention, an oxide coating was vapor deposited using the above-mentioned plasma enhanced chemistry deposition method. The effect of the controlled inner compressive stress in the coating was examined by subjecting some PET samples to an elasticity tensile load during the deposition process.

The coated film was subsequently unloaded, resulting in the well-defined level of the compression in the coating. The adhesion was derived from the classic stress transfer theory of Kelly and Tyson adapted to the geometry of the coating film to model the fragmentation process of the coating during the strain of the polymer substrate. This theory accounts for a Weibull-type coating strength, and introduces a critical stress transfer strength, related to the average coating fragmentation length at fragmentation saturation, which was found to be the most relevant parameter to describe the level of adhesion.

The results of an Evaluation Example according to this invention and a prior arts example in which an oxide coating was vapor-deposited using plasma enhanced chemical vapor deposition method without straining the substrate film, are shown in Fig. 12, respectively. Fig. 12 is a graph showing fragmentation processes of the oxide coating by the plasma CVD in the Evaluation Example according to this invention and the film of the prior arts example.

The crack onset of the film of the present invention (the Evaluation Example) shifted from 4% to 5% (an increase of 25%) as compared to the film of the prior art where no pre-straining is utilized in the coating process. Also, the cohesion force in the carbon-containing silicon oxide layer of the Evaluation Example is 5.7 Gpa as compared to the 4.0 Gpa cohesion force of prior art film, an increase of over 40%. Moreover, the interface shear strength with the substrate film in the carbon-containing silicon oxide layer of the Evaluation Example was 170 GPa as compared to the 100 GPa of the prior art film, an increase of 70%.

Industrial Applicability

Application of the oxide coating film according to this invention may take many forms. Liquid food products such as milk and juices may be packaged in cartons formed from the laminated packaging material of the present invention. The package may be in form of a gable top carton or parallelepiped package. Gable top cartons are formed from precut blanks that are fed to a filling machine. The machine folds the blank and seals the carton, once it is filled with a liquid food product, by closing and sealing the top of the carton. A parallelepiped package, such as the ubiquitous TETRA BRIK® *Aseptic* package, may be formed from a roll of the packaging material on a vertical form, fill and seal machine. The material is formed into a tube, filled by liquid food products, and closed with heat sealing. In both packages, the packaging material is provided with the crease lines to facilitate folding into the final package configuration.

Claims

1. A method for manufacturing a packaging laminate, the method comprising:

straining a substrate film within a range between an upper limit of an initial plastic deformation of the substrate determined by the Young modulus and a lower limit of any improvement of a cohesion force in an oxide coating and an adhesion force between the oxide coating and the substrate film; and

depositing a barrier coating on the substrate film by plasma-enhanced chemical vapor deposition.

2. The method for manufacturing a packaging laminate according to Claim 1 wherein the barrier coating comprises carbon-containing silicon oxide.

3. The method for manufacturing a packaging laminate according to Claim 2 wherein the carbon-containing silicon oxide has a composition formula of SiO_xC_y wherein x is within the range of 1.5-2.2 and y is within the range of 0.15-0.80.

4. The method for manufacturing a packaging laminate according to Claim 1 wherein the substrate film comprises polyethylene terephthalate.

5. The method for manufacturing a packaging laminate according to Claim 2 wherein the cohesion force in the carbon-containing silicon oxide layer is at least 5.7 GPa.